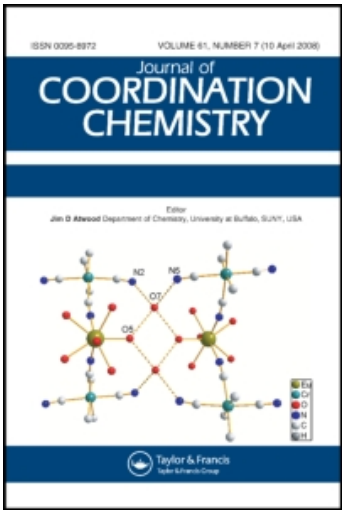

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Synthesis and characterization of novel water-soluble zinc(II) Schiff-base complexes derived from amino acids and salicylaldehyde-5-sulfonates

Davar M. Boghaei[a]; Mehrnaz Gharagozlou[a]
[a] Department of Chemistry, Sharif University of Technology, Tehran, Iran

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Synthesis and characterization of novel water-soluble zinc(II) Schiff-base complexes derived from amino acids and salicylaldehyde-5-sulfonates

DAVAR M. BOGHAEI* and MEHRNAZ GHARAGOZLOU

Department of Chemistry, Sharif University of Technology,
P. O. Box 11365-9516, Tehran, Iran

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New water-soluble zinc(II) Schiff-base complexes derived from amino acids (glycine, L-phenylalanine, and L-valine) and salicylaldehyde-5-sulfonates (sodium salicylaldehyde-5-sulfonate and sodium 3-methoxy-salicylaldehyde-5-sulfonate) have been synthesized. The complexes were characterized by elemental analysis, IR, electronic, ^{1}H NMR, and ^{13}C NMR spectra. In the IR spectra of the complexes, the large difference between the asymmetric ν_{as}(COO) and symmetric ν_s(COO) carboxylate stretch, $\Delta\nu(\nu_{as}(COO)-\nu_s(COO))$ of 199–247 cm^{-1}, indicates monodentate coordination of the carboxylate group. Spectral data showed that in these complexes the ligand is a tridentate ONO moiety, coordinating to the metal through its phenolic oxygen, imine nitrogen, and carboxyl oxygen.

Keywords: Schiff-base complexes; Salicylaldehyde-5-sulfonates; Amino acids; Zn(II) complexes

1. Introduction

Transition metal complexes of Schiff-bases derived from amino acids have received considerable attention due to their biological importance [1–4]. Salicylaldehyde-amino acid Schiff-base complexes are used as non-enzymatic models for the metal-pyridoxal (vitamin B_6) amino acid Schiff-base systems, which are key intermediates in many metabolic reactions of amino acids catalyzed by enzymes which require pyridoxal as a cofactor (transamination, decarboxylation, α and β elimination, racemization, etc.) [5–7]. The coordination of a metal ion to *N*-pyridoxylideneamino acid Schiff-bases stabilizes the azomethine linkage, under conditions that would otherwise promote bond cleavage [8]. Many other roles for pyridoxal phosphate and its Schiff-base complexes have been suggested [9–13] which would indicate that studies of Schiff-base complexes composed of amino acids and salicylaldehyde derivatives may provide useful information to elucidate some of these functions. In addition, complexes of amino acid Schiff-bases are considered to constitute a new kind of potential antibacterial and anticancer reagents [14–16] and Cu(II) N-salicylidene-aminoalkanoato chelate formation has been investigated as a tool for intermolecular cross linking and immobilization

*Corresponding author. Fax: +98 21 66005718. Email: dboghaei@sharif.edu

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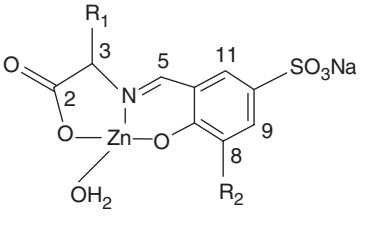
of proteins [17]. Therefore, the synthesis and characterization of non-enzymatic models for the metal-pyridoxal amino acid Schiff-base systems [18], and the design of new *N*-salicylidene aminoalkanoato complexes with antimicrobial [15], anti-inflammatory [19], antipyretic activities together with a superoxide dismutase-like activity [20] have been the driving force for the study of new *N*-salicylidene amino acidato Schiff-base complexes [21].

The model studies of the metal complexes of Schiff-bases composed of pyridoxal phosphate or salicylaldehyde derivatives and amino acids have focused upon the tridentate binding mode of these ligands [22–26]. X-ray crystal structures of these complexes show the ligand to act as a tridentate ONO moiety, coordinating through the phenolato oxygen, imine nitrogen, and carboxylate oxygen [24, 27–29].

Salicylaldehyde-5-sulfonate has been used to prepare the metal complexes of water-soluble Schiff-base ligands by Evans and co-workers [30]. Orvig and co-workers [31] have synthesized water-soluble hexadentate sulfonated amine phenols and also determined stability constants of related Ga and In complexes. Co^{II} complex of the water-soluble tetradentate Schiff base derived from salicylaldehyde-5-sulfonate has also been prepared as an oxygen carrier [32]. Despite the considerable efforts devoted to the preparation of Schiff-base complexes derived from salicylaldehyde and amino acids as non-enzymatic models for pyridoxal-potentiated enzymes [23, 27, 33], there is a lack of information about the preparation of amino acid Schiff-base complexes derived from water-soluble salicylaldehydes, especially from salicylaldehyde-5-sulfonates. In earlier work we synthesized and characterized several Schiff base complexes [34, 35], and performed spectrophotometric studies of the interaction between metal complexes of Schiff-bases and biomolecules [36–38].

Here we report on the preparation and characterization of novel water-soluble zinc(II) Schiff-base complexes (table 1) derived from amino acids (glycine, L-phenylalanine, and L-valine) and salicylaldehyde-5-sulfonates (sodium salicylaldehyde-5-sulfonate and sodium 3-methoxy-salicylaldehyde-5-sulfonate).

Table 1. Water-soluble Zn(II) Schiff-base complexes prepared from amino acids and salicylaldehyde-5-sulfonates.



Compound	R_1	R_2
1a	H	H
2a	CH_2Ph	H
3a	$CH(CH_3)_2$	H
1b	H	OCH_3
2b	CH_2Ph	OCH_3
3b	$CH(CH_3)_2$	OCH_3

2. Experimental

2.1. *Materials and measurements*

All chemicals and solvents were reagent grade, obtained from either Merck or Fluka and used without further purification. Sodium salicylaldehyde-5-sulfonate and sodium 3-methoxy-salicylaldehyde-5-sulfonate were synthesized according to the literature procedure [39] carrying out the sulfonation at 100° and 70°C, respectively.

Elemental analyses were performed using a Heraeus Elemental Analyzer CHN-O-Rapid (Elementar-Analysesysteme, GmbH). Analyses for the metal ions were conducted using a Varian AA-220 spectrophotometer. IR spectra were recorded on a FT-IR JASCO 460 spectrophotometer with KBr pellets. Electronic spectra were recorded using a CARY 100 Bio VARIAN UV-Vis spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker FT-NMR 500 (500 MHz) Ultra Shield spectrometer at ambient temperature in D_2O using tetramethylsilane (TMS) as an internal standard. Melting points were determined on a BUCHI Melting Point B-540.

2.2. *Synthesis of complexes 1a, 2a, and 3a derived from salicylaldehyde-5-sulfonate*

A solution of sodium salicylaldehyde-5-sulfonate (1.12 g, 5 mmol) in 10 cm^3 of water was added to a warm solution (60–70°C) of the corresponding amino acid (5 mmol) in 10 cm^3 of water. The resulting solution was stirred for 30 min. Then a solution of zinc(II) acetate dihydrate (1.11 g, 5 mmol) dissolved in 20 cm^3 water was added dropwise. During the addition, the pH was adjusted to 7 by the addition of 0.5 M NaOH. The solution was stirred vigorously at 60–70°C for 1 h, then concentrated with a rotary evaporator, and left overnight at room temperature. The precipitate obtained was filtered, washed with ethanol and diethyl ether and air-dried. Recrystallization from 5 : 1 v/v ethanol–water resulted in a white precipitate.

^{1}H NMR bands of **1a** (D_2O, ppm): 4.17 (s, 2H), 6.79 (d, 1H), 7.65 (m, 2H), 8.37 (s, 1H). ^{13}C NMR bands of **1a** (D_2O): 51.7, 125.1, 125.5, 132.7, 136.5, 169.1, 179.6, 181.9, 189.6.

^{1}H NMR bands of **2a** (D_2O, ppm): 3.15 (m, 2H), 3.82 (m, 1H), 6.78 (d, 1H), 7.40 (m, 7H), 8.50 (s, 1H). ^{13}C NMR bands of **2a** (D_2O): 51.4, 69.2, 122.4, 126.0, 128.2, 130.1, 135.1, 135.7, 138.3, 151.2, 170.5, 174.6, 179.1, 189.7.

^{1}H NMR bands of **3a** (D_2O, ppm): 1.06 (m, 6H), 2.20 (m, 1H), 3.85 (d, 1H), 6.80 (d, 1H), 7.31 (m, 2H), 8.32 (s, 1H). ^{13}C NMR bands of **3a** (D_2O): 20.8, 21.1, 40.1, 71.8, 124.7, 126.2, 135.6, 140.0, 170.9, 175.1, 179.8, 188.9.

2.3. *Synthesis of complexes 1b, 2b, and 3b derived from 3-methoxy-salicylaldehyde-5-sulfonate*

These complexes were prepared according to the same procedures as those employed for **1a**, **2a**, and **3a** but the Zn(II) complex solution was stirred vigorously at 40–60°C for 90 min.

^{1}H NMR bands of **1b** (D_2O, ppm): 3.66 (s, 3H), 4.01 (s, 2H), 7.11 (s, 1H), 7.23 (s, 1H), 8.21 (s, 1H). ^{13}C NMR bands of **1b** (D_2O): 55.1, 67.9, 125.2, 130.1, 138.7, 172.0, 173.6, 178.2, 180.4, 190.1.

^{1}H NMR bands of **2b** (D_2O, ppm): 3.26 (m, 2H), 3.54 (s, 3H), 3.78 (m, 1H), 7.35 (m, 7H), 8.62 (s, 1H). ^{13}C NMR bands of **2b** (D_2O): 45.3, 59.7, 71.6, 127.5, 128.7, 129.6, 130.0, 137.2, 138.1, 150.4, 175.1, 176.1, 180.1, 182.0, 189.7.

^{1}H NMR bands of **3b** (D_2O, ppm): 1.41 (m, 6H), 2.34 (m, 1H), 3.88 (d, 1H), 7.28 (m, 2H), 8.48 (s, 1H). ^{13}C NMR bands of **3b** (D_2O): 22.2, 22.7, 35.6, 65.2, 66.7, 126.3, 132.7, 134.8, 171.0, 175.6, 177.2, 179.1, 188.8.

3. Results and discussion

The new water-soluble amino acid Schiff-base complexes of Zn(II) were prepared as shown in scheme 1.

The complexes were characterized by elemental analysis, IR, ^{1}H NMR, ^{13}C NMR spectra, and electronic spectra. The analytical data are presented in table 2.

In the IR spectra, all complexes present a broad band due to water centered at approximately 3400 cm^{-1}. A medium band in the range of 2840–2980 cm^{-1} is due to the aliphatic C–H stretch. The Schiff-base structure of the salicylidene-5-sulfonato-amino acidato moiety of the compounds obtained is confirmed by the presence of strong imine ν(C=N) bands occurring in the range 1621–1635 cm^{-1} [40, 41]. The ν_{as}(COO) is related to the strong band appearing in the spectra of the complexes between 1589 and 1599 cm^{-1}, and the symmetric carboxylate stretch, ν_s(COO), corresponds to the

Scheme 1. Synthesis of the water-soluble amino acid Schiff-base complexes of Zn(II).

Table 2. Some properties of the complexes.

Compound	M. p. (°C)	Yield (%)	Elemental analyses calculated (found) (%)			
			C	H	N	Zn
1a	>350	75	28.41	2.65	3.68	17.2
($C_9H_8NO_7SNaZN \cdot H_2O$)			(28.43)	(2.68)	(3.12)	(17.5)
2a	>350	62	39.33	3.71	2.87	13.4
($C_{16}H_{14}NO_7SNaZn \cdot 2H_2O$)			(39.11)	(3.64)	(3.02)	(13.1)
3a	>350	80	32.71	4.12	3.18	14.8
($C_{12}H_{14}NO_7SNaZn \cdot 2H_2O$)			(32.19)	(3.87)	(2.71)	(14.1)
1b	>350	64	28.03	3.29	3.27	15.3
($C_{10}H_{10}NO_8SNaZn \cdot 2H_2O$)			(28.75)	(3.91)	(3.55)	(15.0)
2b	>350	77	38.04	4.13	2.61	12.2
($C_{17}H_{16}NO_8SNaZn \cdot 3H_2O$)			(37.58)	(3.63)	(2.82)	(11.8)
3b	>350	72	34.50	4.01	3.10	14.4
($C_{13}H_{16}NO_8SNaZn \cdot H_2O$)			(35.01)	(3.70)	(2.86)	(14.1)

medium-strong peaks in the range 1343–1390 cm^{-1}. This gives rise to a large difference between ν_{as}(COO) and ν_s(COO), $\Delta\nu(\nu_{as}(COO)–\nu_s(COO))$ of 199–247 cm^{-1}, characteristic of the monodentate coordination of the carboxylate group [42]. The IR spectra of **1b**, **2b**, and **3b** present a strong band around 1250 cm^{-1} which corresponds to the vibration of the phenyl alkyl ether group (Ph–)O(–CH_3) whereas complexes **1a**, **2a**, and **3a** do not show any band in this frequency range. IR spectra of **3a** and **3b** are shown in figure 1.

A medium-strong band at 1520–1540 cm^{-1} is due to the vibration of the (Ph–)C–C(=N) bond [43] and typifies complexes derived from salicylaldehyde [23, 43–45]. Three peaks around 1200, 1100, 1040 cm^{-1} are related to the SO_3^- group [32]. IR spectral data for the complexes are given in table 3.

The electronic spectra, recorded in H_2O solution, show two absorption bands, at approximately 260 nm and 370 nm. The band located at higher energy is probably associated with benzene ring $\pi \rightarrow \pi^*$ [5] transitions. A low energy absorption band

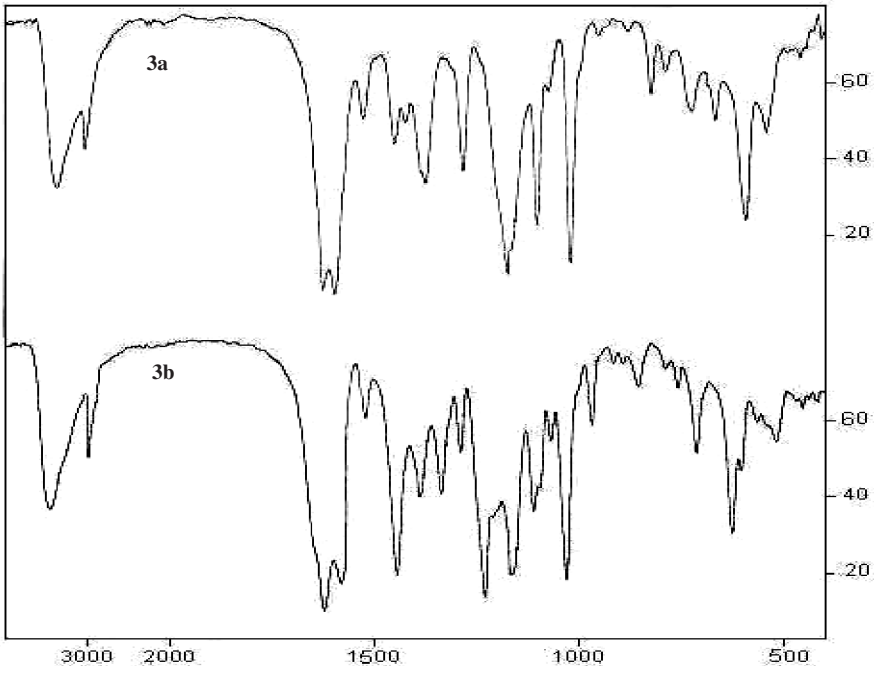


Figure 1. IR spectra of the complexes **3a** and **3b**.

Table 3. The main IR spectral data (cm^{-1}) of the complexes.

Compound	ν(C=N)	ν_{as}(COO)	ν_s(COO)	ν(Ph–O–CH_3)	$\nu(SO_3^-)$
1a	1629	1591	1380	–	1032, 1110, 1170
2a	1621	1589	1390	–	1029, 1109, 1179
3a	1635	1599	1366	–	1047, 1111, 1182
1b	1628	1589	1375	1241	1038, 1113, 1179
2b	1625	1590	1386	1247	1037, 1113, 1178
3b	1632	1590	1343	1250	1042, 1115, 1184

Table 4. Electronic spectral data of the complexes.

Compound	λ, nm (10^{-3} ε, $M^{-1}cm^{-1}$)	
1a	260 (6.1)	367 (2.2)
2a	270 (6.8)	370 (2.4)
3a	262 (8.1)	371 (3.4)
1b	257 (4.2)	370 (2.5)
2b	258 (7.6)	368 (2.8)
3b	260 (3.4)	373 (3.2)

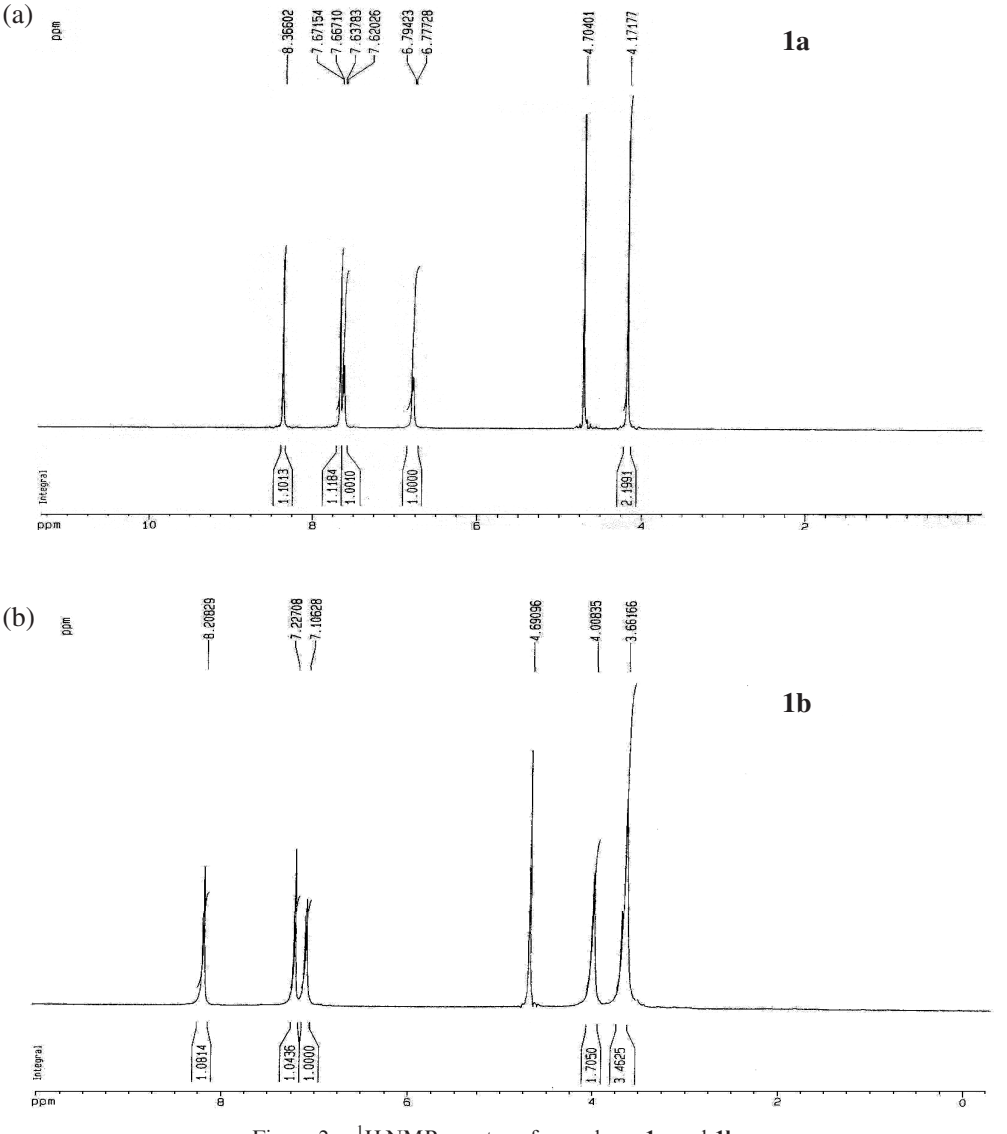


Figure 2. ^{1}H NMR spectra of complexes **1a** and **1b**.

around 370 nm is assigned to a $\pi \rightarrow \pi^*$ transition originating mainly in the azomethine chromophore (imine $\pi \rightarrow \pi^*$ transition) [44–46]. Electronic spectral data for the complexes in H_2O are given in table 4.

In the ^{1}H NMR spectra of the complexes, the HC=N proton appears as a singlet at 8.21–8.62 ppm. In the ^{1}H NMR spectra of the complexes **1a**, **2a**, and **3a** the C(8)–H appears at 6.8 ppm [47] whereas complexes **1b**, **2b**, and **3b** do not show any band at 6.8 ppm as shown in figure 2.

Other aromatic protons were observed at 7.11–7.65 ppm. The C–H proton adjacent to the carboxylate group C(3)–H [47] was observed at 3.78–4.17 ppm.

Elemental analysis, IR, electronic, ^{1}H NMR, and ^{13}C NMR spectral data are in good agreement with previous studies [22–29, 33, 47] which show the presence of a tridentate amino acid Schiff-base ligand coordinating through the phenolato O, imine N, and carboxyl O [24, 27–29]. The carboxylate oxygen atom [47, 48] or the phenolate oxygen [49] of the Schiff base may act as a bridging ligand coordinating to an additional metal ion, producing polymeric structures. The high water-solubility of these complexes may attributed to the sign of the monomeric forms in the aqueous solution, whereas in the solid state it is probable that carboxylate [47, 48] or phenolate [49] oxygen atoms of the Schiff base act as bridging ligands. Studies on the complexes ability to serve as metal-pyridoxal amino acid Schiff-base models as intermediates in enzymatic amino acid transformations, and their reactivity to water exchange by neutral ligands such as pyridine and imidazole to form ternary complexes [50, 51] are in progress.

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